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Arisumi et al.

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(54) **SEMICONDUCTOR MANUFACTURING APPARATUS, LIQUID CONTAINER, AND SEMICONDUCTOR DEVICE MANUFACTURING METHOD**

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(22) Filed: **Feb. 24, 2010**

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Related U.S. Application Data

(62) Division of application No. 11/246,145, filed on Oct. 11, 2005, now abandoned.

(30) **Foreign Application Priority Data**

Oct. 27, 2004 (JP) 2004-311927

(51) **Int. Cl.**
B05D 3/12 (2006.01)

(52) **U.S. Cl.** **427/240**; 427/425; 118/52; 438/758

(58) **Field of Classification Search** 427/240, 427/425; 118/52; 438/758
See application file for complete search history.

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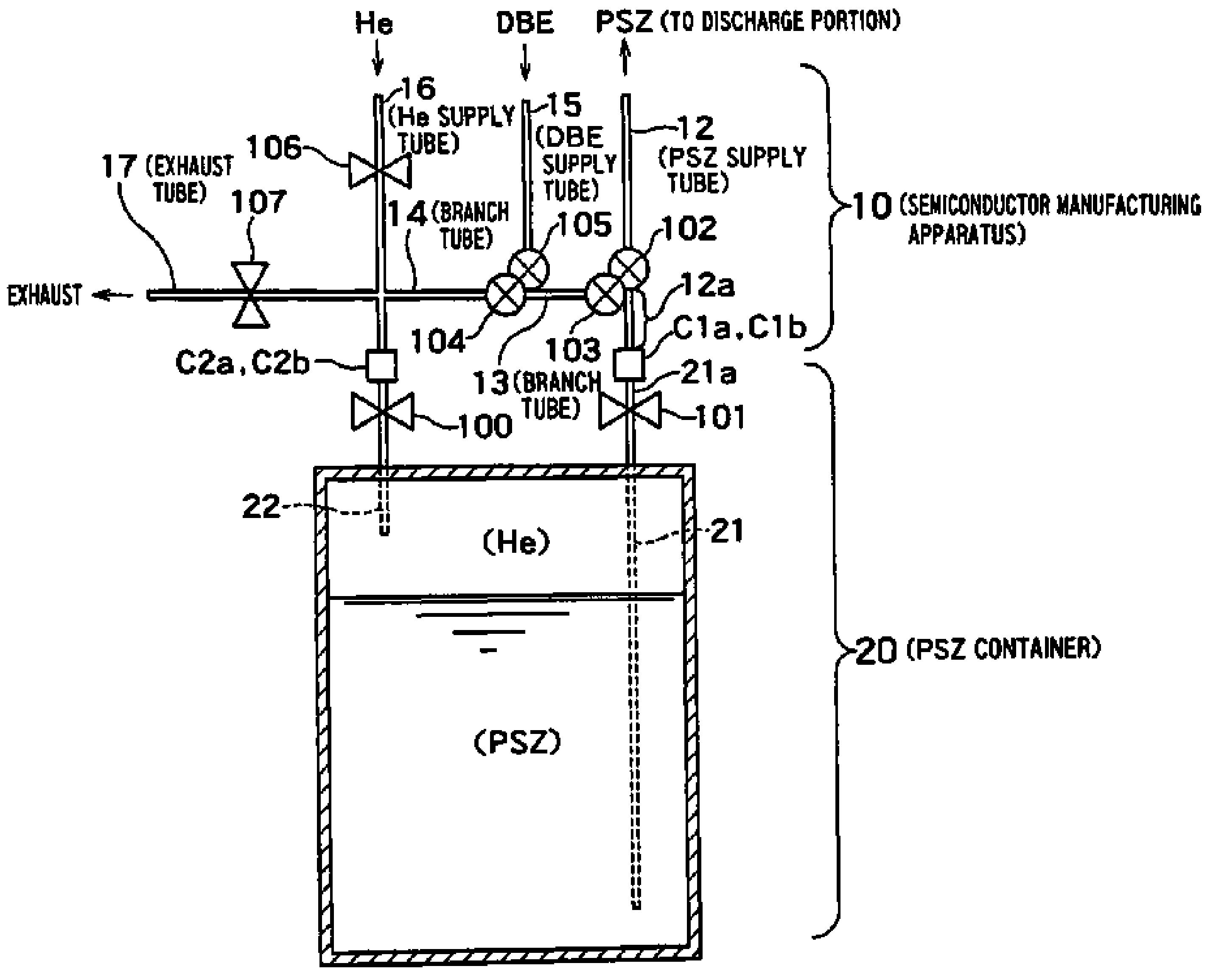
(57) **ABSTRACT**

A semiconductor manufacturing apparatus comprises a discharge portion discharging a coating liquid onto a substrate; a gas supply tube supplying an inert gas into a liquid container that contains the coating liquid, and pressurizing an interior of the liquid container; a coating liquid supply tube airtightly supplying the coating liquid from the liquid container to the discharge portion using pressurization from the gas supply tube; a first connecting portion capable of attaching and detaching the liquid container to and from the coating liquid supply tube; a second connecting portion capable of attaching and detaching the liquid container to and from the gas supply tube; and a solvent supply tube supplying a solvent, which can dissolve the coating liquid, to the first connecting portion.

6 Claims, 13 Drawing Sheets



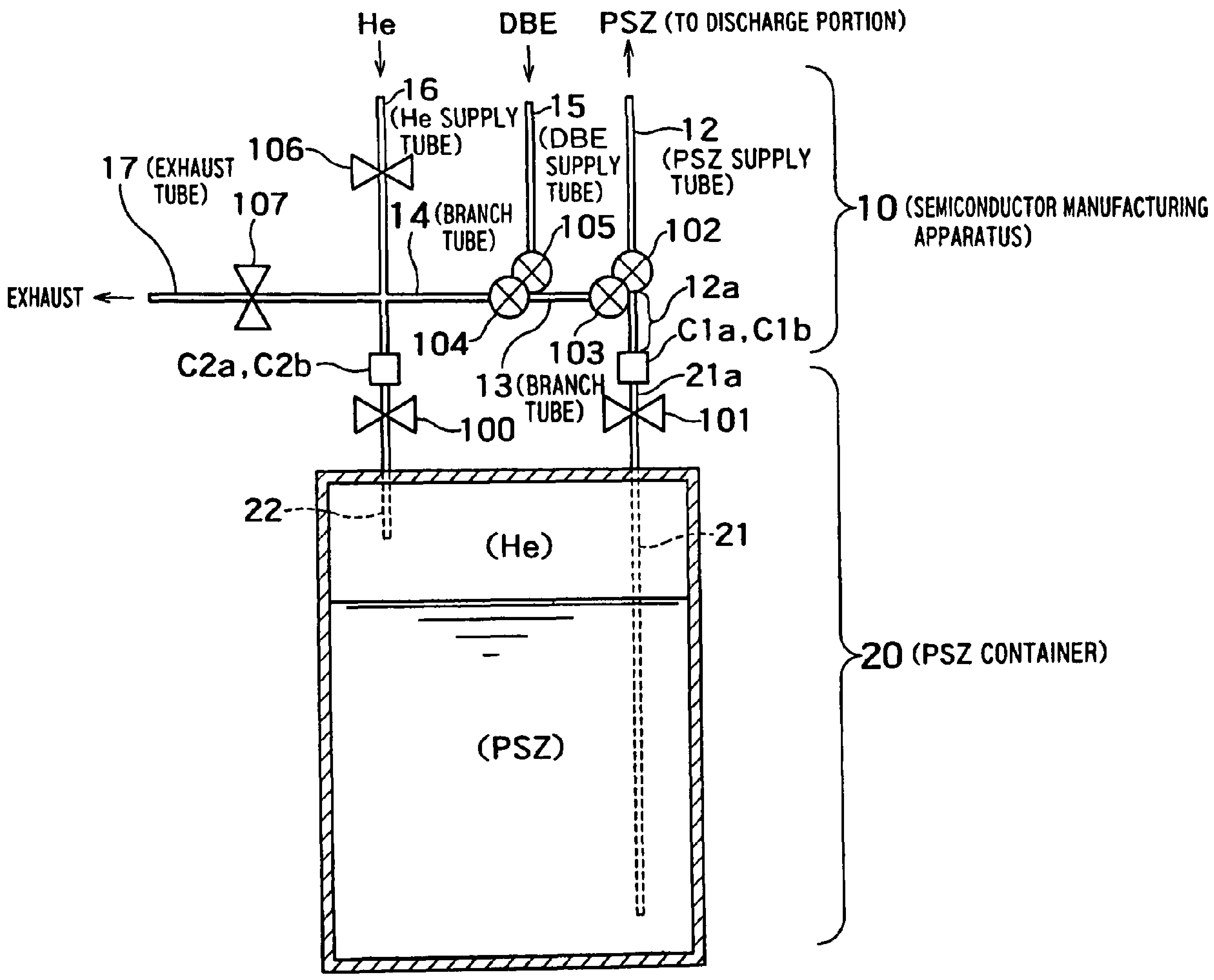

He
DBE
PSZ (TO DISCHARGE PORTION)
16 (He SUPPLY TUBE)
15 (DBE SUPPLY TUBE)
12 (PSZ SUPPLY TUBE)
17 (EXHAUST TUBE)
106
107
14 (BRANCH TUBE)
105
102
10 (SEMICONDUCTOR MANUFACTURING APPARATUS)
EXHAUST
12a
C1a, C1b
104
103
C2a, C2b
13 (BRANCH TUBE)
21a
100
101
22
(He)
21
20 (PSZ CONTAINER)
(PSZ)

FIG. 1

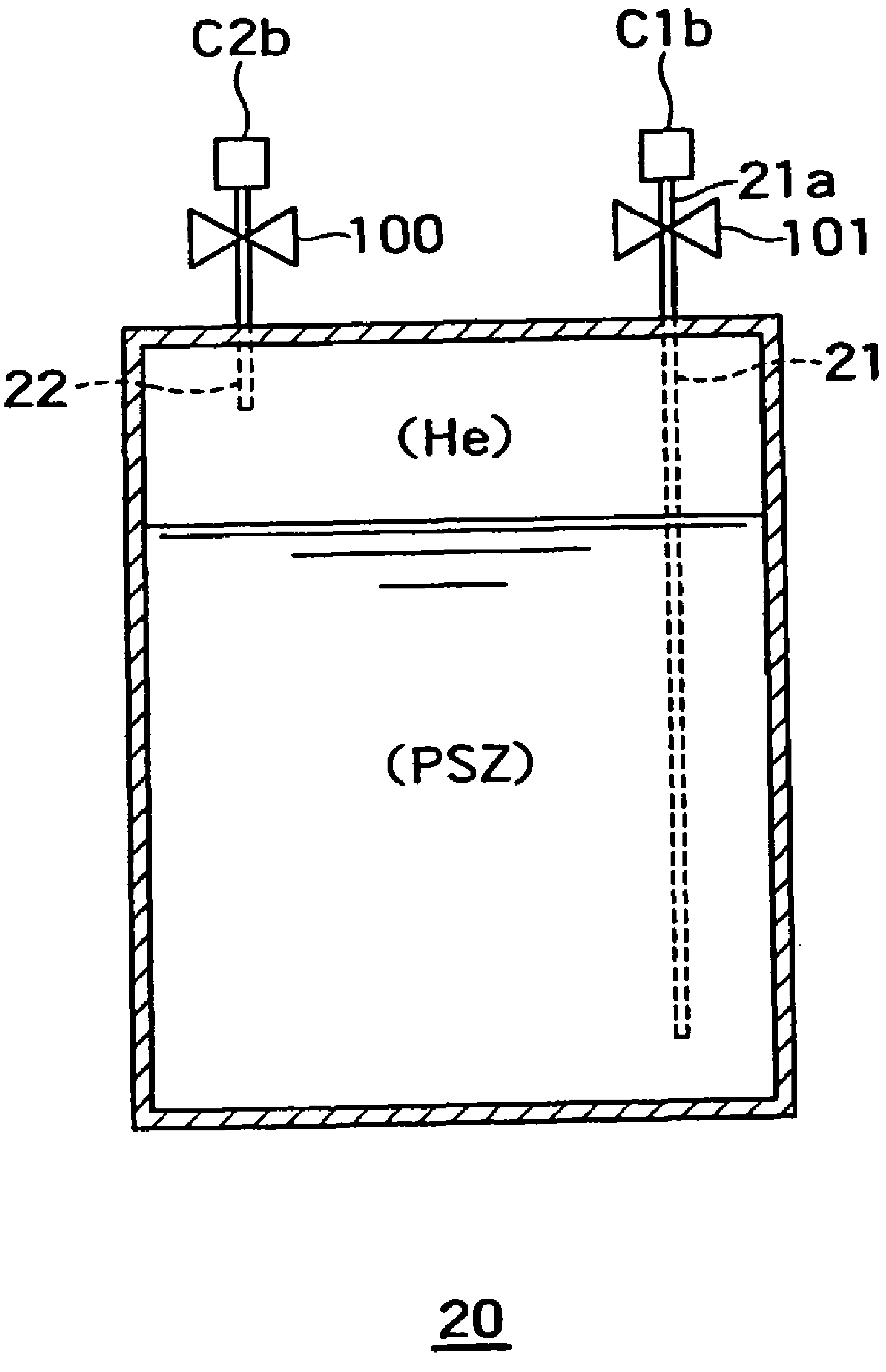


FIG. 2

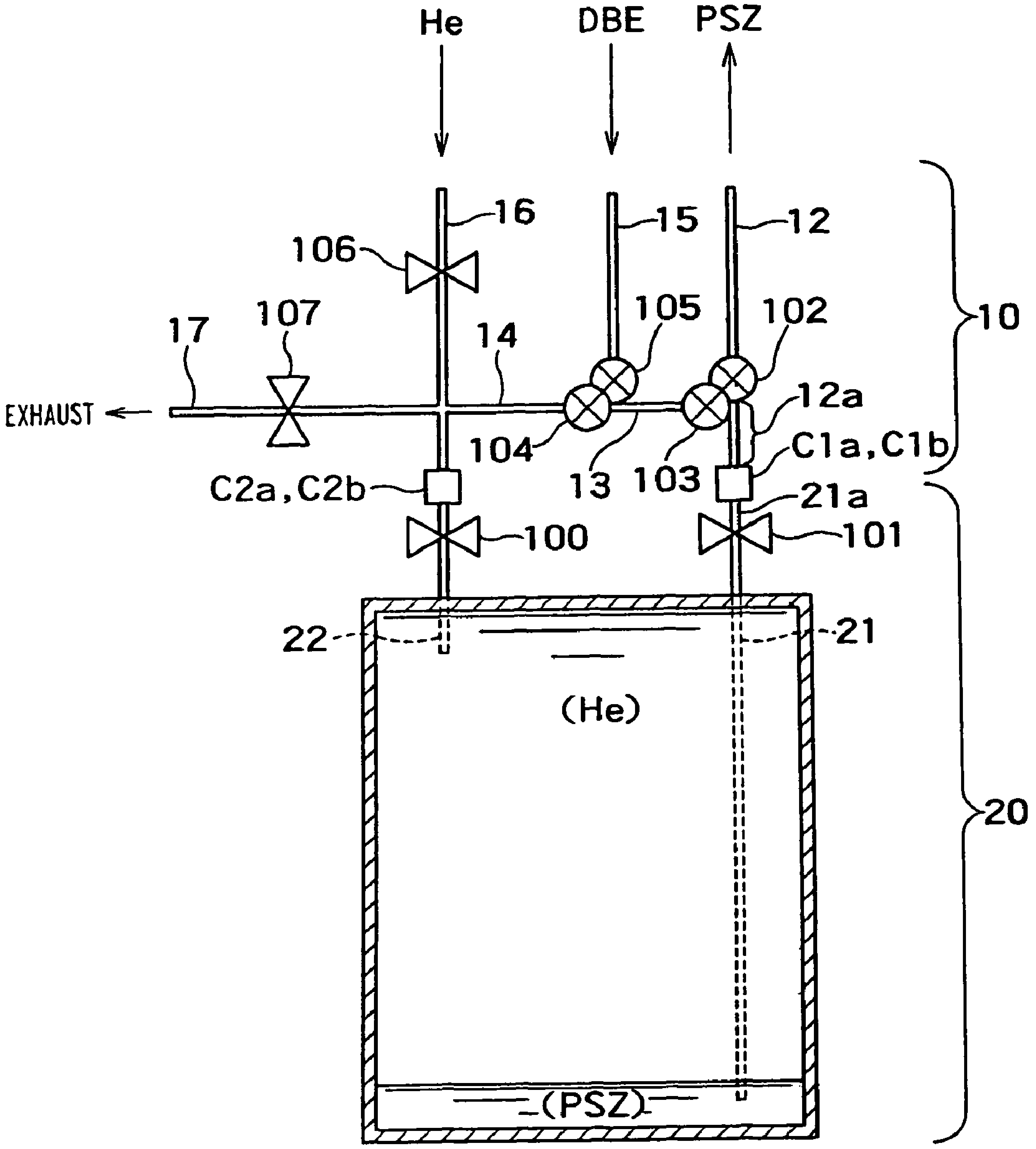

He
DBE
PSZ
16
15
12
106
105
102
10
17
107
14
EXHAUST
12a
104
13
103
C1a,C1b
C2a,C2b
21a
100
101
22
21
(He)
20
(PSZ)

FIG. 3

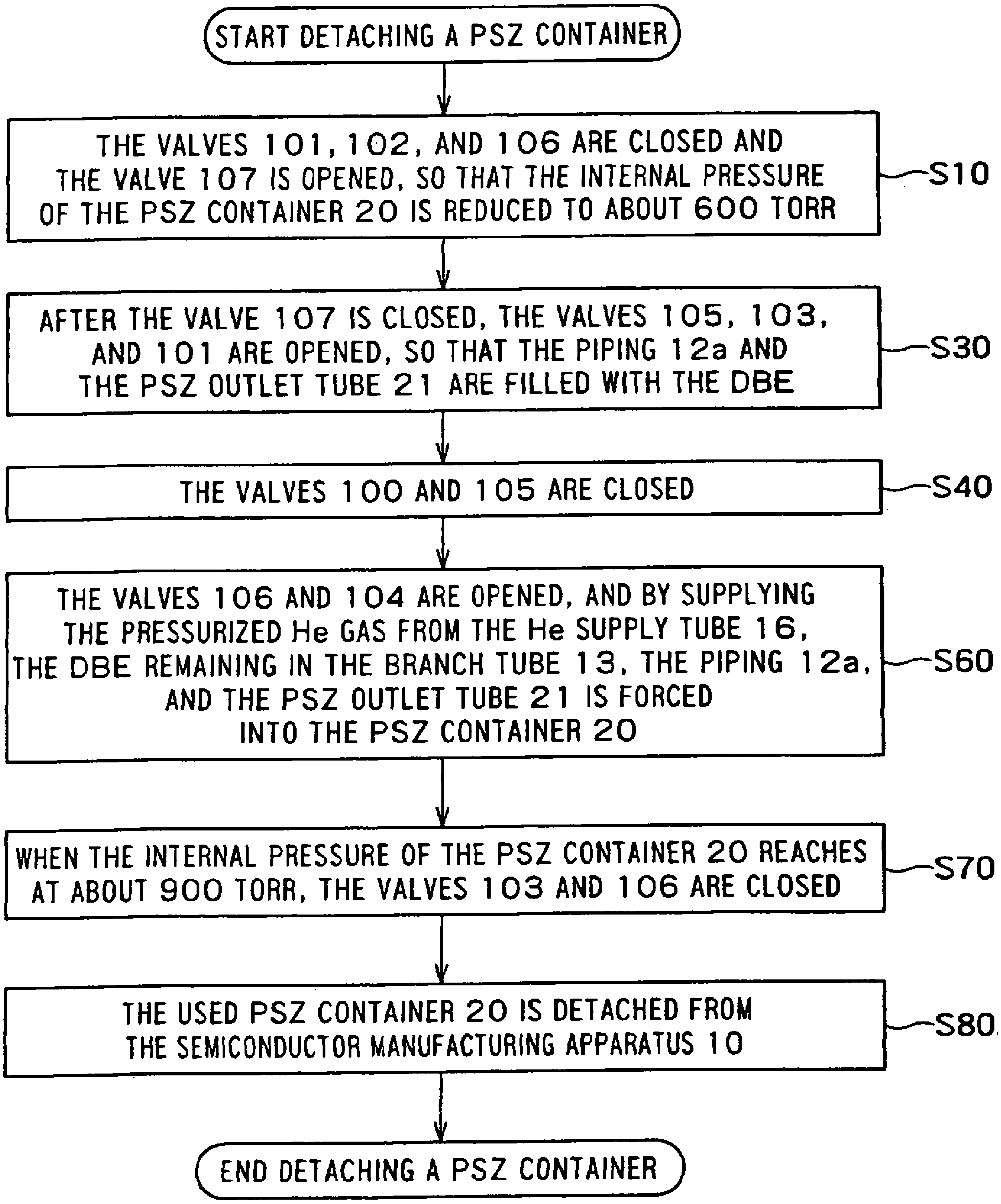

START DETACHING A PSZ CONTAINER
THE VALVES 101, 102, AND 106 ARE CLOSED AND THE VALVE 107 IS OPENED, SO THAT THE INTERNAL PRESSURE OF THE PSZ CONTAINER 20 IS REDUCED TO ABOUT 600 TORR
S10
AFTER THE VALVE 107 IS CLOSED, THE VALVES 105, 103, AND 101 ARE OPENED, SO THAT THE PIPING 12a AND THE PSZ OUTLET TUBE 21 ARE FILLED WITH THE DBE
S30
THE VALVES 100 AND 105 ARE CLOSED
S40
THE VALVES 106 AND 104 ARE OPENED, AND BY SUPPLYING THE PRESSURIZED He GAS FROM THE He SUPPLY TUBE 16, THE DBE REMAINING IN THE BRANCH TUBE 13, THE PIPING 12a, AND THE PSZ OUTLET TUBE 21 IS FORCED INTO THE PSZ CONTAINER 20
S60
WHEN THE INTERNAL PRESSURE OF THE PSZ CONTAINER 20 REACHES AT ABOUT 900 TORR, THE VALVES 103 AND 106 ARE CLOSED
S70
THE USED PSZ CONTAINER 20 IS DETACHED FROM THE SEMICONDUCTOR MANUFACTURING APPARATUS 10
S80
END DETACHING A PSZ CONTAINER

FIG. 4

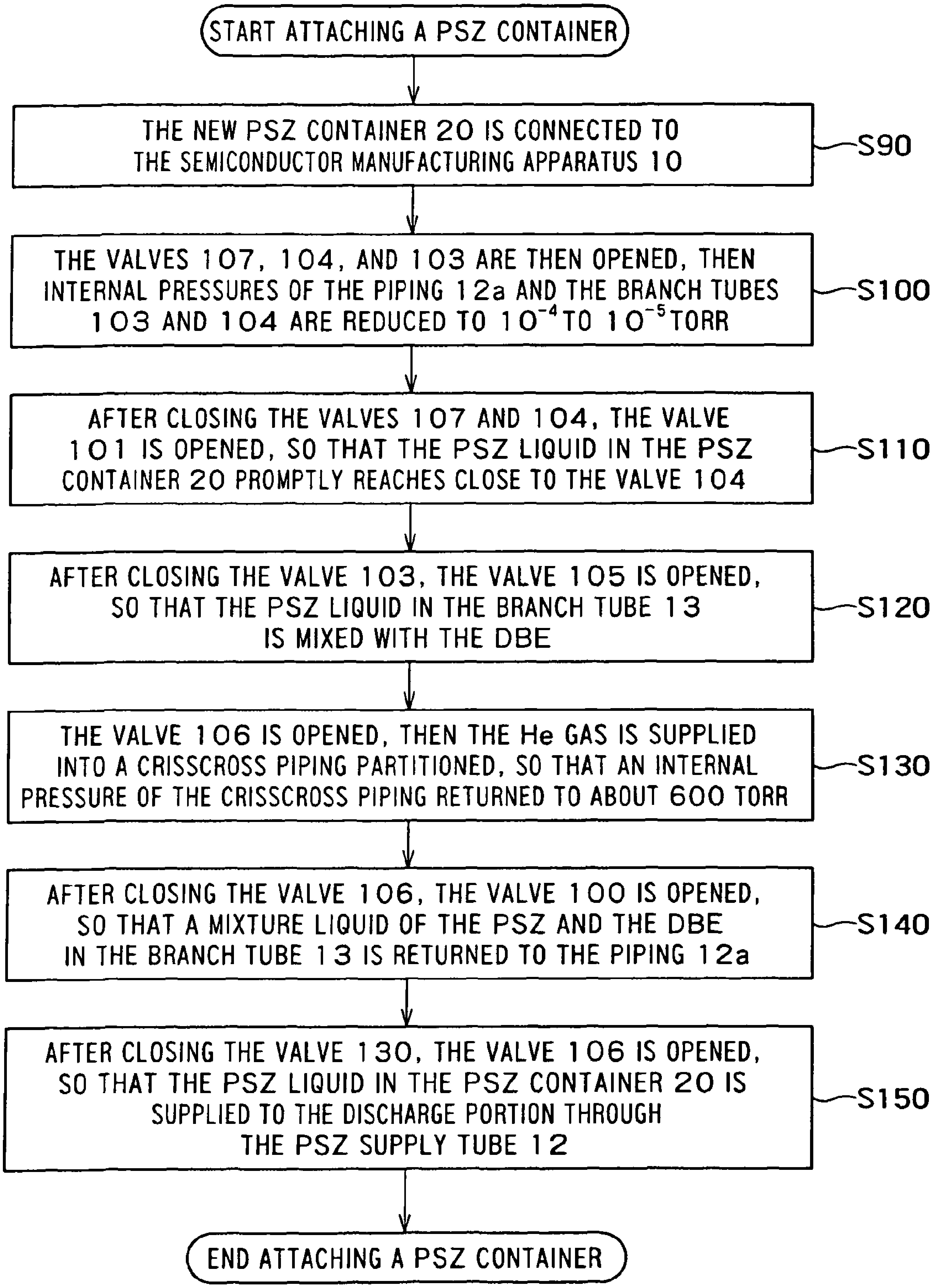

START ATTACHING A PSZ CONTAINER
THE NEW PSZ CONTAINER 20 IS CONNECTED TO THE SEMICONDUCTOR MANUFACTURING APPARATUS 10
S90
THE VALVES 107, 104, AND 103 ARE THEN OPENED, THEN INTERNAL PRESSURES OF THE PIPING 12a AND THE BRANCH TUBES 103 AND 104 ARE REDUCED TO 10^{-4} TO 10^{-5} TORR
S100
AFTER CLOSING THE VALVES 107 AND 104, THE VALVE 101 IS OPENED, SO THAT THE PSZ LIQUID IN THE PSZ CONTAINER 20 PROMPTLY REACHES CLOSE TO THE VALVE 104
S110
AFTER CLOSING THE VALVE 103, THE VALVE 105 IS OPENED, SO THAT THE PSZ LIQUID IN THE BRANCH TUBE 13 IS MIXED WITH THE DBE
S120
THE VALVE 106 IS OPENED, THEN THE He GAS IS SUPPLIED INTO A CRISSCROSS PIPING PARTITIONED, SO THAT AN INTERNAL PRESSURE OF THE CRISSCROSS PIPING RETURNED TO ABOUT 600 TORR
S130
AFTER CLOSING THE VALVE 106, THE VALVE 100 IS OPENED, SO THAT A MIXTURE LIQUID OF THE PSZ AND THE DBE IN THE BRANCH TUBE 13 IS RETURNED TO THE PIPING 12a
S140
AFTER CLOSING THE VALVE 130, THE VALVE 106 IS OPENED, SO THAT THE PSZ LIQUID IN THE PSZ CONTAINER 20 IS SUPPLIED TO THE DISCHARGE PORTION THROUGH THE PSZ SUPPLY TUBE 12
S150
END ATTACHING A PSZ CONTAINER

FIG. 5

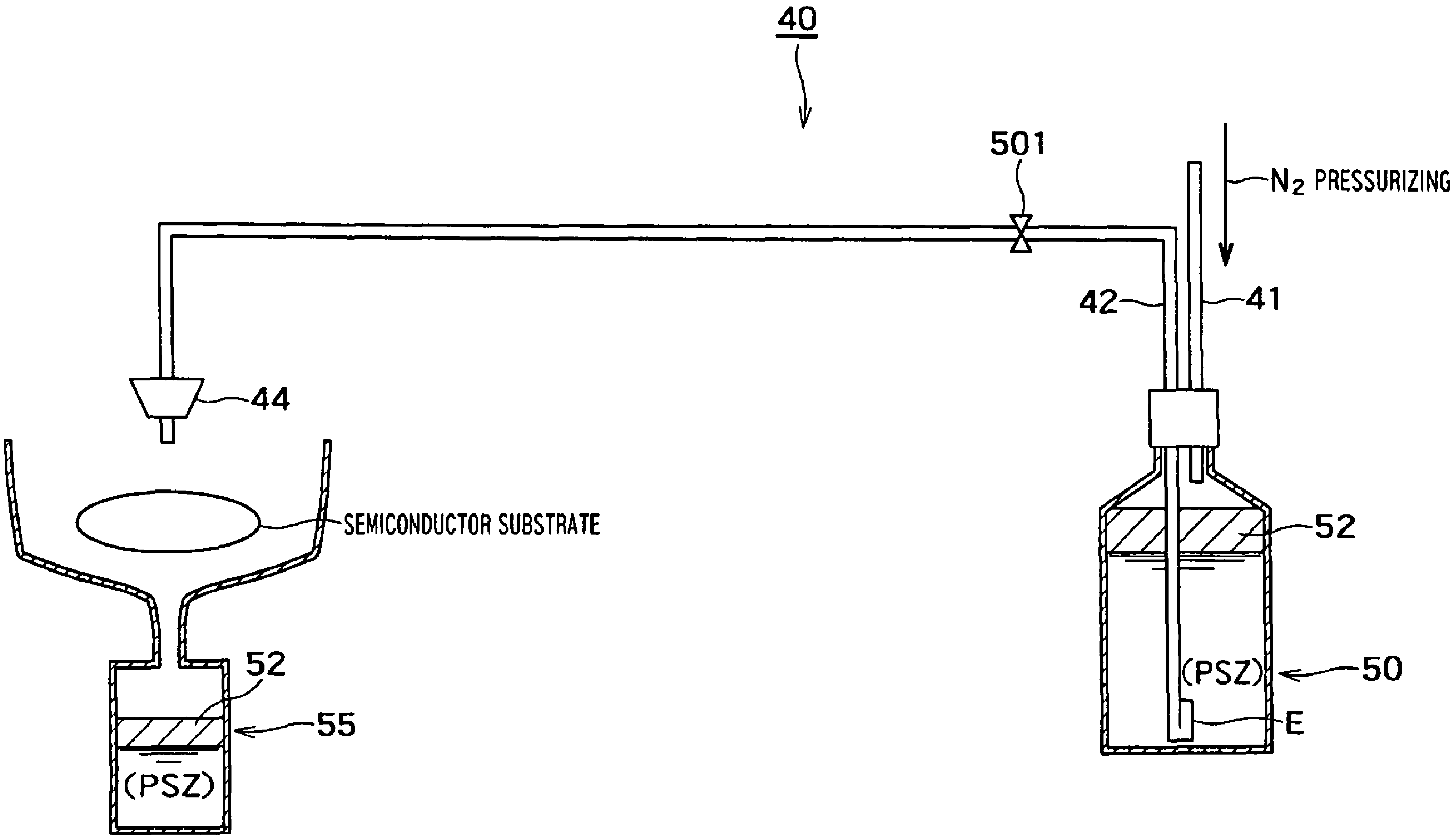

40
501
N_2 PRESSURIZING
42
41
44
SEMICONDUCTOR SUBSTRATE
52
52
55
(PSZ)
(PSZ)
50
E

FIG. 6

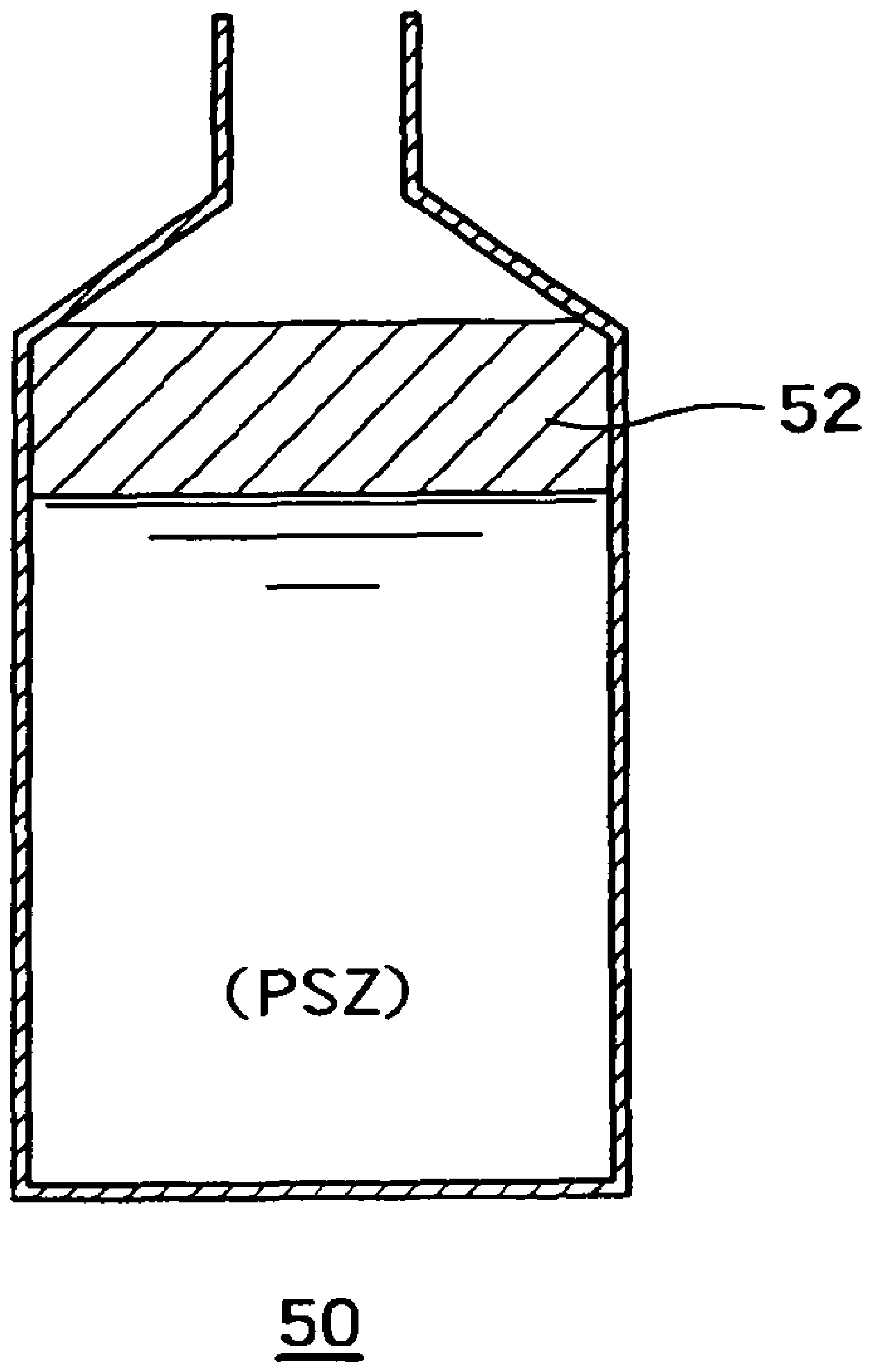


FIG. 7

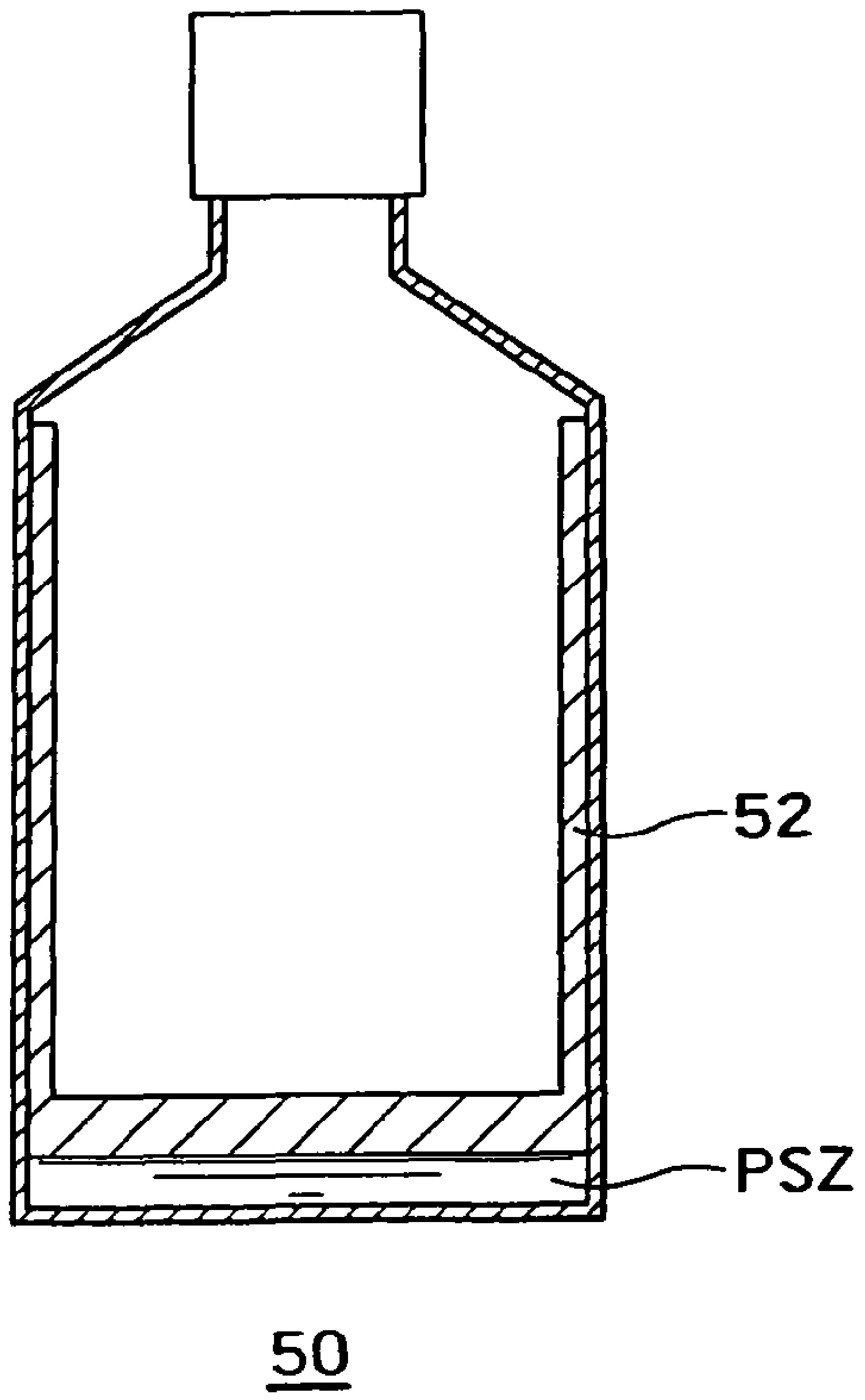


FIG. 8

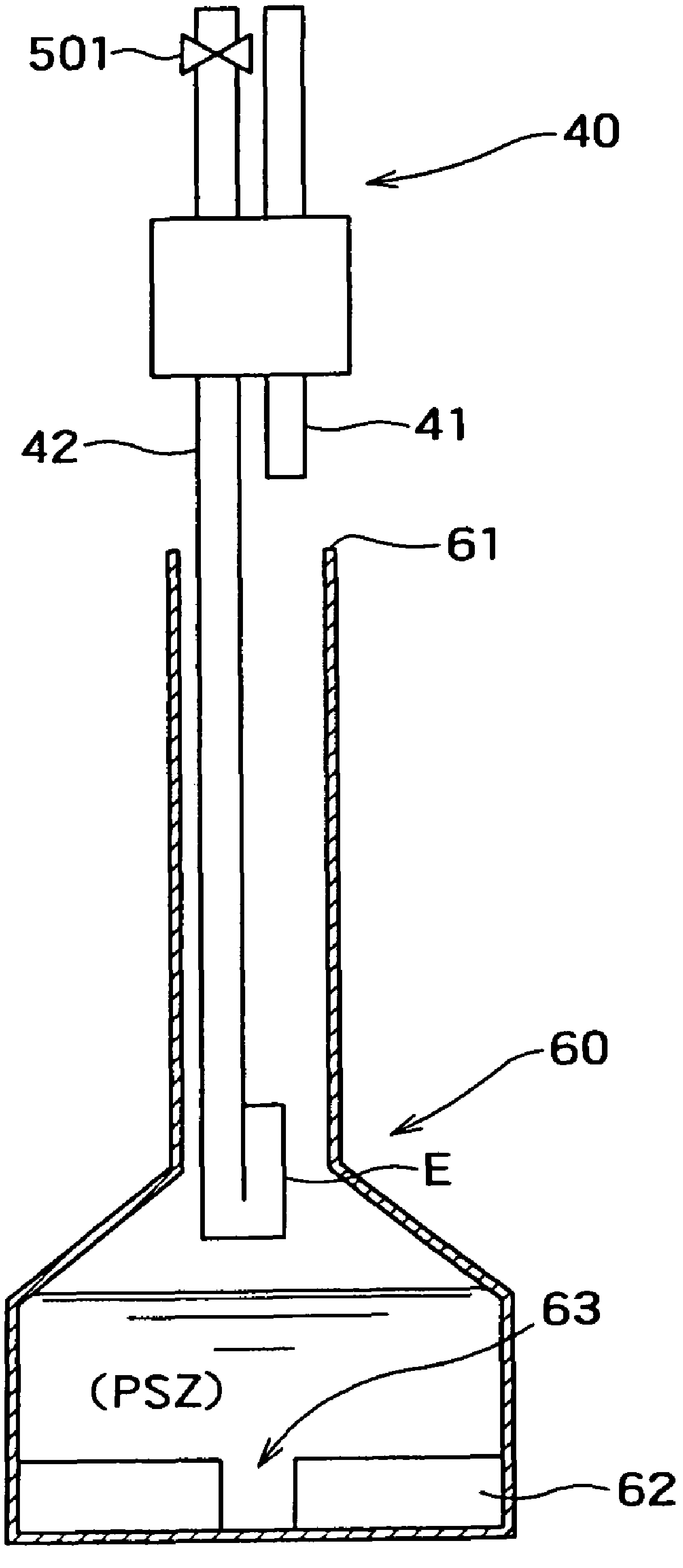


FIG. 9

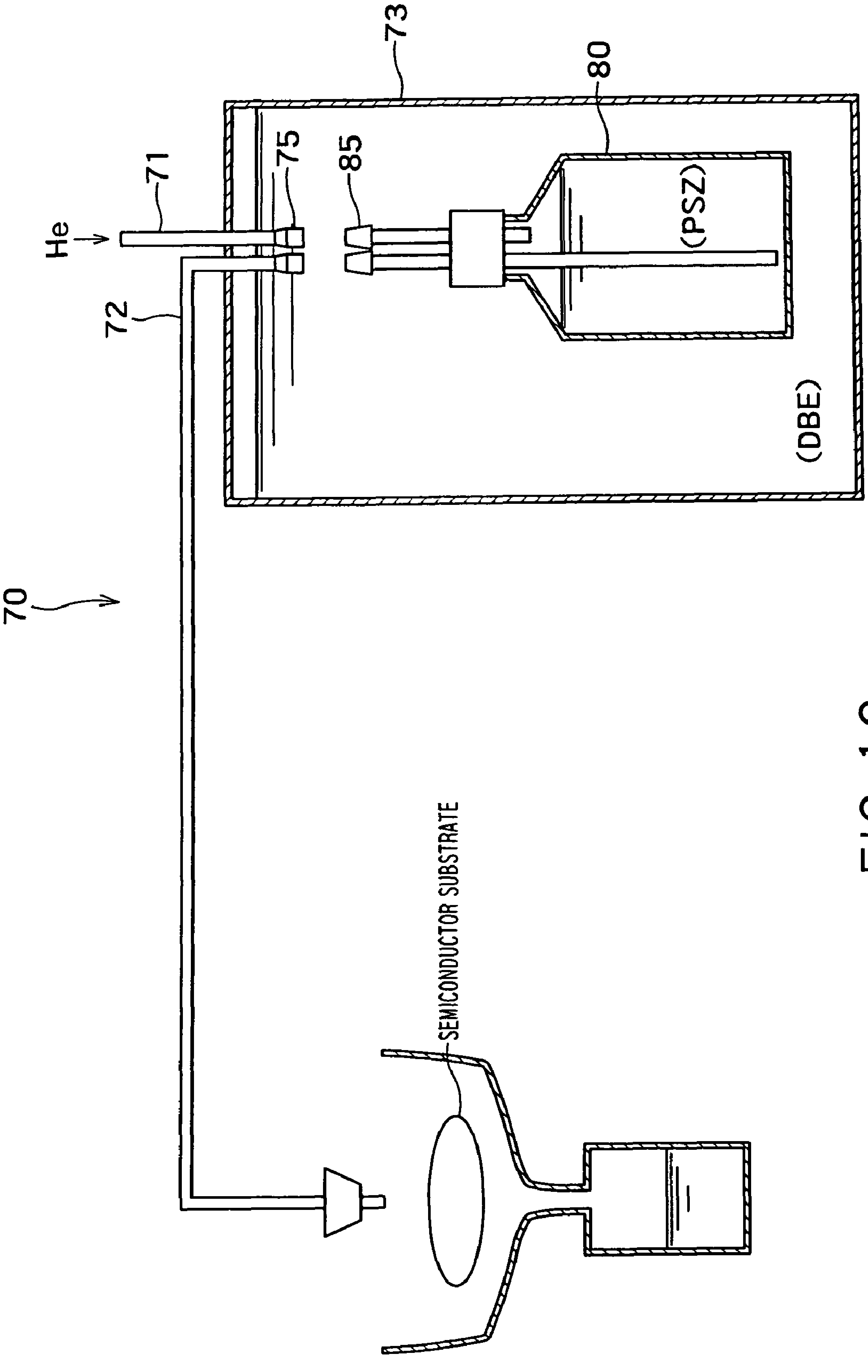


FIG. 10

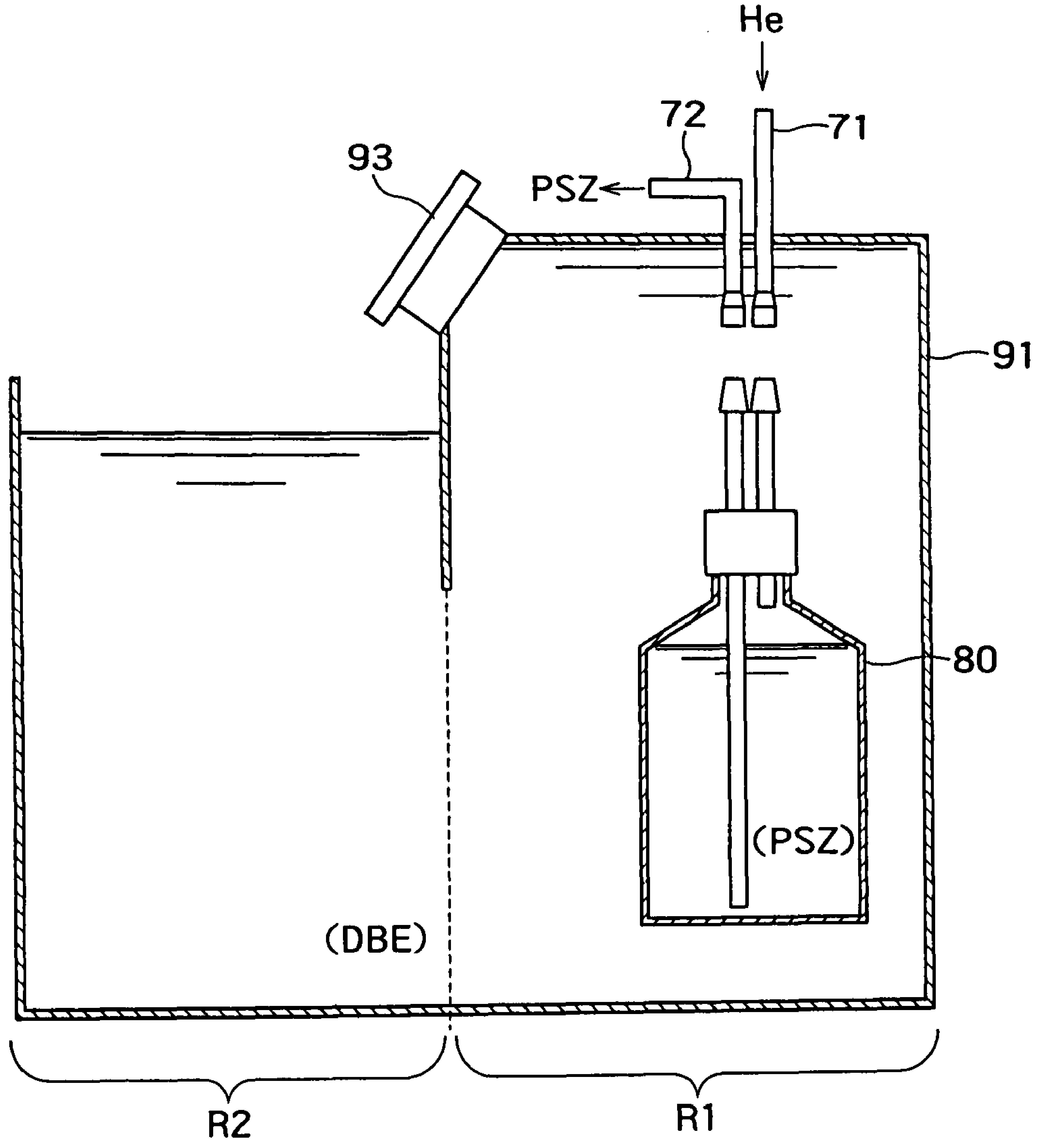


FIG. 11

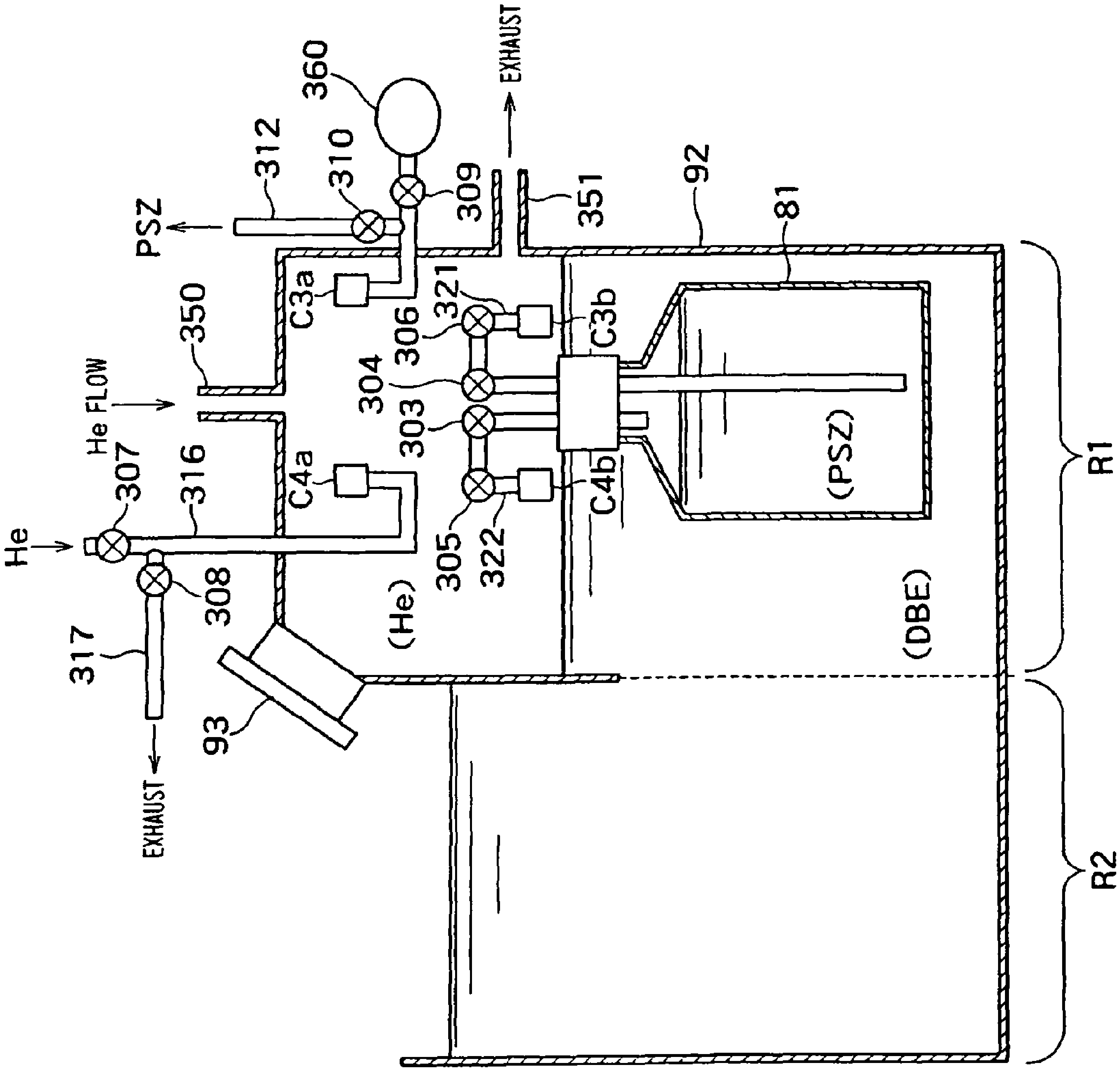

He
307
316
He FLOW
350
C4a
C3a
PSZ
312
310
309
360
EXHAUST
351
92
81
321
306
304
303
305
322
C3b
C4b
(PSZ)
(He)
(DBE)
308
317
EXHAUST
93
R1
R2

FIG. 12

	THE NUMBERS OF PARTICLES HAVING VARIOUS PARTICLE DIAMETERS				
	0.2~0.4 [μm]	0.4~0.6 [μm]	0.6~0.8 [μm]	0.8~1.0 [μm]	AT LEAST 1.0 [μm]
THE CONVENTIONAL TECHNIQUE (FIG.12)	477	45	13	5	20
THE FIRST EMBODIMENT	0	0	0	0	0
THE SECOND AND THE THIRD EMBODIMENTS	0	1	0	0	0
THE FOURTH TO SIXTH EMBODIMENTS	1	0	0	0	0

FIG. 13

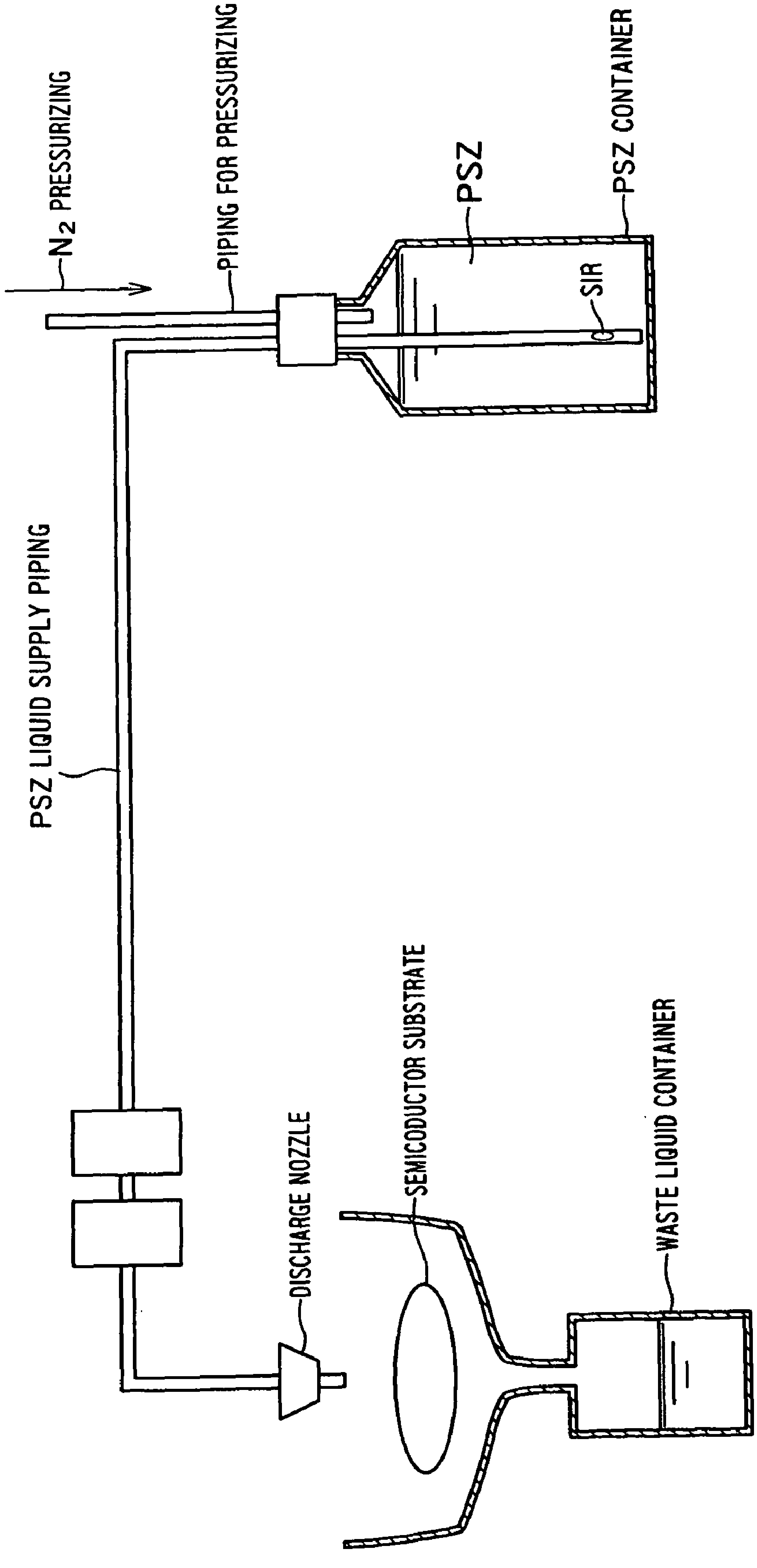

N_2 PRESSURIZING
PIPING FOR PRESSURIZING
PSZ
PSZ CONTAINER
SIR
PSZ LIQUID SUPPLY PIPING
DISCHARGE NOZZLE
SEMICODUCTOR SUBSTRATE
WASTE LIQUID CONTAINER

FIG. 14

SEMICONDUCTOR MANUFACTURING APPARATUS, LIQUID CONTAINER, AND SEMICONDUCTOR DEVICE MANUFACTURING METHOD

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional of application Ser. No. 11/246,145, filed Oct. 11, 2005 now abandoned, and is based upon and claims the benefit of priority from the prior Japanese Patent Application No. 2004-311927, filed on Oct. 27, 2004, the entire contents of both of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a semiconductor manufacturing apparatus, a liquid container and a semiconductor device manufacturing method.

2. Related Art

A semiconductor device such as a NAND flash memory is required to bury a silicon oxide film in a trench having a high aspect ratio so as to form deep STI (shallow trench isolation) in a narrow region.

To meet this demand, a film formation technique for using both an HDP (high density plasma) film and an SOG (spin on glass) film has been developed (see Japanese Patent No. 3178412). According to this technique, a silicon oxide film is deposited by HDP-CVD (chemical vapor deposition), and a film coated with a perhydropolysilazane liquid (hereinafter, “PSZ (Polysilazane)”) is coated on the silicon oxide film by spin coating. The coated film is then silicified by a cure treatment. It is thereby possible to bury the silicon oxide film in a trench having a high aspect ratio.

FIG. **14** is a conceptual view showing a conventional SOG step. Normally, a bottled PSZ liquid filled with nitrogen is commercially available. When a bottle cap is opened at a time of a used PSZ bottle being replaced by a new one, the air never fails to enter the bottles. In addition, during the replacement, the air may possibly enter a PSZ liquid supply nozzle from a tip end of the PSZ liquid supply nozzle. If so, the PSZ liquid unavoidably contacts with the air.

The PSZ developed to be silicified at a temperature as low as about several hundred Celsius (° C.) can react with water and oxygen as represented by Chemical Formula 1, and can be solidified even at a room temperature when being exposed to the atmosphere.

$$—(SiH_2NH)_n—+2nO \rightarrow nSiO_2+nNH_3 \quad \text{(Formula 1)}$$

When the PSZ is solidified in a piping from a PSZ container to a discharge nozzle, the solidified PSZ fixedly adheres onto a semiconductor substrate after being discharged together with the PSZ-coating liquid, thereby disadvantageously causing bulges, divots, and streaks. Even if the solidified PSZ is not formed, the air mixed into the piping and discharged onto the semiconductor substrate as air bubbles may possibly cause the bulges, divots, and streaks. Furthermore, the solidified PSZ may possibly damage the semiconductor substrate and a polishing cloth or cause a contamination during CMP (Chemical Mechanical Polish) process.

When the PSZ remains in the used container, the PSZ reacts with water and oxygen to generate ammonium (NH_3) and silane (SiH_4). The ammonium and silane bring about considerably serious environmental and safety problems. It is, therefore, difficult to manage and handle the PSZ and the PSZ container in manufacturing of semiconductor products.

In these circumstances, therefore, a semiconductor manufacturing apparatus, which airtightly transports a liquid to be coated on a substrate from a container to a discharge portion and suppresses the liquid from coming in contact with the air when the container is replaced by another one, has been desired.

Furthermore, a liquid container detachable from the semiconductor manufacturing apparatus, which airtightly transports the liquid to be coated on the substrate from the container to the discharge portion and suppresses the liquid from coming in contact with the air when the container is replaced by another one, has been desired.

SUMMARY OF THE INVENTION

A semiconductor manufacturing apparatus according to an embodiment of the present invention comprises a discharge portion discharging a coating liquid onto a substrate; a gas supply tube supplying an inert gas into a liquid container that contains the coating liquid, and pressurizing an interior of the liquid container; a coating liquid supply tube airtightly supplying the coating liquid from the liquid container to the discharge portion using pressurization from the gas supply tube; a first connecting portion capable of attaching and detaching the liquid container to and from the coating liquid supply tube; a second connecting portion capable of attaching and detaching the liquid container to and from the gas supply tube; and a solvent supply tube supplying a solvent, which can dissolve the coating liquid, to the first connecting portion.

A semiconductor manufacturing apparatus according to an embodiment of the present invention comprises a discharge portion discharging a coating liquid onto a substrate; a gas supply tube supplying an inert gas into a liquid container that contains the coating liquid, and pressurizing an interior of the liquid container; a coating liquid supply tube airtightly supplying the coating liquid from the liquid container to the discharge portion using pressurization from the gas supply tube; a first connecting portion capable of attaching and detaching the liquid container to and from the coating liquid supply tube; a second connecting portion capable of attaching and detaching the liquid container to and from the gas supply tube; and a liquid bath including the solvent capable of dissolving the coating liquid,

wherein the first connecting portion and the second connecting portion are present in the liquid bath.

A liquid container according to an embodiment of the present invention which contains a coating liquid and which is undesirable to expose to the atmosphere before utilizing for semiconductor manufacturing, the liquid container being attachable to or detachable from a semiconductor manufacturing apparatus, wherein

the liquid container seals a coating liquid and a protection liquid, which is lower specific gravity than that of the coating liquid and does not react with the coating liquid, in a pressurized atmosphere with an inert gas higher than the atmospheric pressure.

A semiconductor manufacturing method using a semiconductor manufacturing apparatus according to an embodiment of the present invention comprises a discharge portion discharging a coating liquid onto a substrate; a gas supply tube pressurizing an interior of the liquid container with an inert gas; a coating liquid supply tube airtightly supplying the coating liquid from the liquid container to the discharge portion using pressurization from the gas supply tube; a first connecting portion capable of attaching and detaching the liquid container to and from the coating liquid supply tube; a second connecting portion capable of attaching and detaching the liquid container to and from the gas supply tube; and an exhaust tube capable of reducing an internal pressure of the coating liquid supply tube including the first connecting portion:

the method comprising:

attaching the liquid container to the first connecting portion and the second connecting portion;

supplying the inert gas to the liquid container via the gas supply tube, thereby carrying the coating liquid to the discharge portion via the coating liquid supply tube;

discharging the coating liquid to the substrate from the discharge portion;

reducing an internal pressure of the liquid container via the exhaust tube and the second connecting portion after discharging the coating liquid; and

returning the coating liquid in the first connecting portion and the liquid supply tube to the liquid container by using the pressure in the liquid container.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic diagram of a semiconductor manufacturing apparatus and a PSZ container according to a first embodiment of the present invention;

FIG. **2** shows a PSZ container **20**;

FIG. **3** shows an operation for detaching the PSZ container **20**;

FIG. **4** is a flowchart that shows a flow of an operation for detaching the PSZ container **20**;

FIG. **5** is a flowchart that shows a flow of an operation for attaching the PSZ container **20**;

FIG. **6** is a schematic diagram of a semiconductor manufacturing apparatus and a PSZ container according to a second embodiment of the present invention;

FIG. **7** is a cross-sectional view of a PSZ container according to the second embodiment;

FIG. **8** is a cross-sectional view of a PSZ container according to the second embodiment;

FIG. **9** is a cross-sectional view of a PSZ container according to a third embodiment of the present invention;

FIG. **10** is a schematic diagram of a semiconductor manufacturing apparatus and a PSZ container according to a fourth embodiment of the present invention;

FIG. **11** is a schematic diagram of a semiconductor manufacturing apparatus and a PSZ container according to a fifth embodiment of the present invention;

FIG. **12** is a schematic diagram of a semiconductor manufacturing apparatus and a PSZ container according to a sixth embodiment of the present invention;

FIG. **13** is a table that shows effects of the respective embodiments of the present invention; and

FIG. **14** is a schematic diagram showing a conventional SOG step.

DETAILED DESCRIPTION OF THE INVENTION

Hereafter, exemplary embodiments of the present invention will be described more specifically with reference to the drawings. Note that the invention is not limited to the embodiments.

First Embodiment

FIG. **1** is a schematic diagram of a semiconductor manufacturing apparatus **10** and a PSZ container **20** according to a first embodiment of the present invention. The semiconductor manufacturing apparatus **10** is an apparatus for dropping a PSZ liquid from a discharge nozzle onto a semiconductor substrate, and spreading the PSZ liquid on the semiconductor substrate by spin coating at an SOG step.

The semiconductor manufacturing apparatus **10** includes a coating liquid discharge portion (not shown), a PSZ supply tube **12** serving as a coating liquid supply tube, a dibutyl ether supply tube (hereinafter, "DBE supply tube") **15** serving as a solvent supply tube, a helium supply tube (hereinafter, "He supply tube") **16** serving as a gas supply tube, an exhaust tube **17**, and branch tubes **13** and **14**. Since the discharge portion may be identical to the discharge nozzle shown in FIG. **14**, it is not shown in FIG. **1**.

The semiconductor manufacturing apparatus **10** also includes a connector C**1***a* serving as a first connecting portion and a connector C**2***a* serving as a second connecting portion. The PSZ supply tube **12** is connected to the connector C**1***a* through a valve **102**. One end of the branch tube **13** is connected to the PSZ supply tube **12** between the valve **102** and the connector C**1***a* through a valve **103**. The other end of the branch tube **13** is connected to one end of the branch tube **14** through a valve **104**, and also connected to the DBE supply tube **15** through a valve **105**.

The He supply tube **16** is connected to the connector C**2***a* through a valve **106**. The other end of the branch tube **14** is connected to the He supply tube **16** between the valve **106** and the connector C**2***a*, and the exhaust tube **17** is connected to the He supply tube **16** through a valve **107**. A vacuum pump, e.g., a turbomolecular pump, not shown, is connected to the exhaust pipe **17**.

As shown in FIG. **2**, the PSZ container. **20** includes a pair of connectors C**1***b* and C**2***b* connectable to the connectors C**1***a* and C**2***a* of the semiconductor manufacturing apparatus **10**, respectively. The PSZ container **20** can be thereby attached to or detached from the PSZ supply tube **12** and the He supply tube **16**.

The PSZ container **20** also includes a PSZ outlet tube **21** provided from the connector C**1***b* to neighborhoods of a bottom of the container **20**, and a He inlet tube **22** provided from the connector C**2***b* to neighborhoods of an upper surface of the container **20**. Valves **101** and **100** are provided at the PSZ outlet tube **21** near the connector C**1***b* and the He inlet tube **22** near the connector C**2***b*, respectively, whereby an interior of the PSZ container **20** is shut off from the atmosphere.

The PSZ container **20** is withdrawn in a sealed state after usage and recyclable by filling a PSZ liquid again into the container **20**. An inert gas as well as the PSZ liquid is filled into the PSZ container **20** with the inert gas pressurized at a slightly higher pressure than an atmospheric pressure. By doing so, the air is not mixed into the PSZ container **20**. The PSZ liquid is contained in the PSZ container **20** up to a portion near the valve **100** but contained so as not to reach the valve **100**. It is thereby possible to prevent air bubbles from being generated in the PSZ liquid. The PSZ liquid is contained in the PSZ container **20** in a state, for example, in which the PSZ liquid is dissolved into a solvent such as dibutyl ether (hereinafter, "DBE").

The inert gas filled into the PSZ container **20** is preferably the same as the inert gas, i.e., helium gas supplied to the semiconductor manufacturing apparatus **10** for the following reasons. The helium possesses a property that it is insoluble with an organic solvent such as the PSZ or DBE, and the helium is less expensive than the other inert gas such as xenon. The PSZ container **20** and the semiconductor manufacturing apparatus **10** are preferably made of stainless steel (SUS). However, the material for the PSZ container **20** and the semiconductor manufacturing apparatus **10** is not limited to SUS but may be an arbitrary material that has good airtightness, that does not react with the PSZ, and that does not cause a metal contamination.

(PSZ Supply Operation)

When the PSZ liquid is supplied to the discharge portion, the PSZ supply tube **12** and the He supply tube **16** are used but the DBE supply tube **15** and the exhaust tube **17** are not used. Due to this, the valves **100**, **101**, **102**, and **106** are open whereas the valves **103**, **104**, **105**, and **107** are closed. In this state, the He supply tube **16** supplies the He gas to the PSZ container **20** to pressurize an interior of the PSZ container **20**. An internal atmospheric pressure of the PSZ container **20** is made thereby higher than a surrounding atmospheric pressure, so that the PSZ liquid is supplied to the discharge portion through the PSZ supply tube **12**. At this time, the PSZ supply tube **12** airtightly supplies the PSZ liquid from the PSZ container **20** to the discharge portion. The discharge portion discharges the coating liquid onto the semiconductor substrate (see FIG. **14**).

(PSZ Container Detachment Operation)

FIG. **3** shows a manner of detaching the PSZ container **20** from the semiconductor manufacturing apparatus **10**. FIG. **4** is a flowchart that shows a flow of an operation for detaching the PSZ container **20**. With reference to FIGS. **3** and **4**, the operation for detaching the PSZ container **20** will be described.

When the PSZ liquid is supplied to the discharge portion and a residual amount of the PSZ liquid in the PSZ container **20** is small, it is necessary to replace the PSZ container **20** by a new PSZ container **20**. At this time, if the valves **100**, **101**, **102**, and **106** are simply closed to disconnect the connector C**1***a* from the connector C**1***b* and the connector C**2***a* from the connector C**2***b*, the PSZ liquid remaining in the PSZ supply tube **12** from the connector C**1***a* to the valve **102** may possibly come in contact with the air.

To prevent this contact, when the PSZ container **20** is detached, the valves **101**, **102**, and **106** are closed in this order and the valve **107** is opened (at a step S**10**). At this step, since the valves **100** and **107** are open, the exhaust pipe **17** communicates with the PSZ container **20** while the valves other than the valves **100** and **107** are closed. The internal pressure of the PSZ container **20** is thereby reduced to about 600 Torr through the exhaust tube **17** (at a step S**10**).

After the valve **107** is closed, the valves **105**, **103**, and **101** are opened in this order. At this time, the internal pressure of the PSZ container **20** is lower than the atmospheric pressure (about 760 Torr). Due to this, DBE is supplied into the PSZ container **20** through the DBE supply tube **15**, the branch tube **13**, the PSZ supply tube from the valve **102** to the connector C**1***a* (hereinafter, the PSZ supply tube **12** in this section will be referred to as "piping **12***a*"), and the PSZ outlet tube **21**. The PSZ liquid remaining in the piping **12***a* and the PSZ outlet tube **21** is thereby forced into the PSZ container **20**. At the same time, the piping **12***a* and the PSZ outlet tube **21** are filled with the DBE (at a step S**30**).

After the internal pressure of the PSZ container **20** is identical to the atmospheric pressure, the valves **100** and **105** are closed (at a step S**40**). The valves **106** and **104** are then opened in this order. The He supply tube **16** thereby communicates with the PSZ container **20** through the branch tubes **14** and **13**. By supplying the pressurized He gas from the He supply tube **16**, the DBE remaining in the branch tube **13**, the piping **12***a*, and the PSZ outlet tube **21** is forced into the PSZ container **20** (at a step S**60**). When the internal pressure of the PSZ container **20** reaches at about 900 Torr, the valves **103** and **106** are closed (at a step S**70**). Thereafter, the connector C**1***a* is disconnected from the connector C**1***b*, and the connector C**2***a* is disconnected from the connector C**2***b*, and the used PSZ container **20** is detached from the semiconductor manufacturing apparatus **10** (at a step S**80**).

Since the He gas at the higher pressure than the atmospheric pressure is filled into the used PSZ container **20**, the air is not mixed into the PSZ container **20**. It is, therefore, possible to prevent oxygen and water from reacting with the PSZ liquid in the PSZ container **20**.

When the used PSZ container **20** is detached from the semiconductor manufacturing apparatus **10**, the PSZ supply tube **12** from the valve **102** to the discharge portion is filled with the PSZ liquid. The piping **12***a* and a piping (hereinafter, "piping **21***a*") from the connector C**1***b* of the PSZ container **20** to the valve **101** are exposed to the atmosphere. In this embodiment, however, the piping **12***a* is washed by the DBE used as the solvent for the PSZ liquid in the PSZ container **20**, no PSZ liquid remains in the piping **12***a*. Therefore, no PSZ solid matter is generated in the pipings **12***a* and **21***a*.

(PSZ Container Attachment Operation)

FIG. **5** is a flowchart that shows a flow of an operation for attaching the PSZ container **20** to the semiconductor manufacturing apparatus **10**. With reference to FIGS. **1** and **5**, an operation for attaching the new PSZ container **20** to the apparatus **10** will be described.

Although no PSZ liquid is contained in the piping **21***a* of the new PSZ container **20**, the piping **21***a* is exposed to the atmosphere. Due to this, it is necessary to take care not to contact the air present in the pipings **12***a* and **21***a* with the PSZ liquid.

The new PSZ container **20** is connected to the semiconductor manufacturing apparatus **10** (at a step S**90**). At this time, all the valves **100** to **107** are closed. The valves **107**, **104**, and **103** are then opened in this order. Internal pressures of the piping **12***a* and the branch tubes **103** and **104** are reduced to 10^{-4} to 10^{-5} Torr (at a step S**100**).

After closing the valves **107** and **104** in this order, the valve **101** is opened. At this time, a piping including the piping **12***a* from the valve **101** to the valve **103** and the branch tube **13** are in a low pressure state close to a vacuum. Therefore, the PSZ liquid in the PSZ container **20** promptly reaches close to the valve **104** (at a step S**110**).

After closing the valve **103**, the valve **105** is opened. The PSZ liquid in the branch tube **13** is thereby mixed with the DBE (at a step S**120**).

Next, the valve **106** is opened, the He gas is supplied into a crisscross piping partitioned by the valves **100**, **107**, **106**, and **104**, and an internal pressure of the crisscross piping is thereby returned to about 600 Torr (at a step S**130**). After closing the valve **106**, the valve **100** is opened. At this time, the internal pressure of the crisscross piping partitioned by the valves **100**, **107**, **106**, and **104** is slightly lower than the atmospheric pressure. Due to this, a mixture liquid of the PSZ, and the DBE in the branch tube **13** is returned to at least the piping **12***a* (at a step S**140**). Since the DBE liquid is used as the solvent for the PSZ liquid in the PSZ container **20**, no problem occurs even if a small amount of the mixture liquid enters the PSZ container **20**. It is noted that He air bubbles are sometimes mixed into this mixture liquid of the PSZ and the DBE.

After closing the valve **103**, the valve **106** is opened (at a step S**150**). The PSZ liquid in the PSZ container **20** can be thereby supplied to the discharge portion through the PSZ supply tube **12**. Since the initially supplied liquid is either the mixture liquid of the PSZ and the DBE or the mixture liquid containing the He air bubbles, the liquid is disposed of.

When the amount of the PSZ liquid in the PSZ container **20** is reduced, the detachment operation and the attachment operation for detaching and attaching the PSZ container **20** are repeatedly carried out according to the steps S**10** to S**150**. As described above, according to the first embodiment, the PSZ liquid can be supplied to the discharge portion without exposure to the air.

In recent years, following an increase in the aspect ratio of STI, it has been difficult to bury the silicon oxide film in the trench. The STI in the NAND flash memory is, in particular, high in aspect ration as compared with a logic circuit, and required to bury the silicon oxide film in a non-tapered trench.

When the present embodiment is applied, such defects as bumps, divots, and streaks can be prevented even at manufacturing steps of a NAND flash memory with a trench having an opening width of, for example, 90 to 70 nm. This can contribute to an improvement in the yield of semiconductor devices.

Furthermore, in the used PSZ container **20**, the residual liquid does not contact with the atmosphere and no hazardous and ignitable gas such as ammonium or silane is generated.

The valves **102** to **105** are preferably gate valves, e.g., block valves, without any excessive space at branch portions.

Second Embodiment

FIG. **6** is a schematic diagram of a semiconductor manufacturing apparatus **40** and a PSZ container **50** according to a second embodiment of the present invention. The semiconductor manufacturing apparatus **40** differs from the semiconductor manufacturing apparatus shown in FIG. **14** in that a tip end of a PSZ supply tube **42** is formed into a "J" shape. The other constituent elements of the semiconductor manufacturing apparatus **40** may be identical to those of the semiconductor manufacturing apparatus shown in FIG. **14**. The PSZ container **50** contains not only a PSZ liquid but also a protection liquid **52** that shuts off the PSZ liquid from the atmosphere. The other constituent elements of the PSZ container **50** may be identical to those of the PSZ container shown in FIG. **14**.

In the semiconductor manufacturing apparatus shown in FIG. **14**, an end of the PSZ supply tube is directed downward. Due to this, when the PSZ container is attached to the semiconductor manufacturing apparatus, air bubbles tend to be mixed into the PSZ supply tube. When the air bubbles are oxygen or water bubbles, they may disadvantageously cause the PSZ liquid to be solidified. When the air bubbles are inert gas bubbles such as helium bubbles, the PSZ liquid is disadvantageously difficult to discharge from the discharge portion.

In the semiconductor manufacturing apparatus **40** according to the second embodiment, by contrast, an end of the PSZ supply tube **42** is directed upward. This can make it more difficult to mix air bubbles into the PSZ supply tube **42** when the PSZ container **50** is attached to the semiconductor manufacturing apparatus **40**. It is noted that the PSZ container **50** is attached to the semiconductor manufacturing apparatus **40** after a valve **501** is closed. By doing so, even while the PSZ container **50** is being attached to the apparatus **40**, the PSZ liquid remains at the tip end of the PSZ supply tube **42**.

FIGS. **7** and **8** are cross-sectional views of the PSZ container **50** according to the second embodiment. FIG. **7** shows the PSZ container **50** when being attached to the semiconductor manufacturing apparatus **40**, and FIG. **8** shows the PSZ container **50** when being detached from the semiconductor manufacturing apparatus **40**.

Desirable conditions for the protection liquid **52** that covers the PSZ in the PSZ container **50** are: no reaction with the PSZ liquid (condition 1), lower specific gravity than that of the PSZ liquid and no mixture with the PSZ liquid (condition 2), higher wettability with an inner wall of the PSZ container **50** than that of the PSZ liquid (condition 3), and non-inclusion of carbon (C) in impurities (condition 4). The conditions 1 and 2 are necessary conditions. Examples of a material that satisfies the conditions 1 and 2 include straight-chain-hydrocarbon and cyclic cyclohexane.

When the protection liquid **52** satisfies the conditions 1 and 2, the protection liquid **52** can cover a liquid level of the PSZ liquid in the PSZ container **50**. When the protection liquid **52** satisfies the conditions 3, the protection liquid **52** can cover the inner wall of the PSZ container **50** and the residual PSZ liquid tends to reside on a bottom of the PSZ container **50** as shown in FIG. **8**. It is thereby possible to ensure that the PSZ liquid is shut off from the atmosphere. The condition 4 is intended to eliminate carbon that may have a conductive type of either p or n as much as possible.

In the second embodiment, when the new PSZ container **50** is attached to the semiconductor manufacturing apparatus **40**, the air enters the PSZ container **50**. However, since the protection liquid **52** covers the surface of the PSZ, it is possible to prevent contact of the PSZ with the air. Further, when the used PSZ container **50** is detached from the semiconductor manufacturing apparatus **40**, it is possible to prevent the contact of the PSZ liquid with the air since the protection film **52** covers the surface of the PSZ. In addition, while the PSZ liquid is being supplied, the liquid level of the PSZ is lowered. However, since the protection liquid **52** has a favorable wettability, the protection liquid **52** even covers the surface of the PSZ adhering to the inner wall of the PSZ container **50**.

As shown in FIG. **8**, even if the PSZ container **50** is temporarily held at a different location, the air in the PSZ container **50** does not contact with the PSZ liquid and no ammonium or silane is, therefore, generated in the PSZ container **50**.

When the PSZ container **50** is attached to the semiconductor manufacturing apparatus **40**, the protection liquid **52** enters the PSZ supply tube **42**. However, since the specific gravity of the protection liquid **52** is lower than that of the PSZ liquid and the tip end of the PSZ supply tube **42** is J-shaped and directed upward, the protection liquid **52** surfaces on the tip end of the PSZ supply tube **42**. Therefore, the protection liquid **52** is not supplied to a discharge portion **44**.

In the second embodiment, the protection liquid **52** may be also used in a waste liquid container provided below a spin coater. If so, a waste liquid is thereby out of contact with the air. The second embodiment is, therefore, more preferable in environmental and safety aspects.

The semiconductor manufacturing apparatus **40** and the PSZ container **50** according to the second embodiment are relatively inexpensive and can be realized by simple changes in designs of the conventional semiconductor manufacturing apparatus and the conventional PSZ container, respectively.

Third Embodiment

FIG. **9** is a cross-sectional view of a semiconductor manufacturing apparatus **40** and a PSZ container **60** according to a third embodiment of the present invention. The PSZ container **60** according to the third embodiment includes a narrow opening portion **61** and a concave portion **63** that can accept a J-shaped tip end E of a PSZ supply tube **42**. The semiconductor manufacturing apparatus **40** is identical to the semiconductor manufacturing apparatus **40** according to the second embodiment.

According to the third embodiment, since the opening portion **61** is narrow, an area by which a PSZ liquid contacts with the air can be made small. In addition, by inserting the tip end E of the PSZ supply tube **42** into the concave portion **63**, the PSZ liquid can be made most use of to the end.

The semiconductor manufacturing apparatus **40** and the PSZ container **60** according to the third embodiment are also relatively inexpensive and can be realized by simple changes in designs of the conventional semiconductor manufacturing apparatus and the conventional PSZ container, respectively.

Fourth Embodiment

FIG. **10** is a schematic diagram of a semiconductor manufacturing apparatus **70** and a PSZ container **80** according to a fourth embodiment of the present invention. The semiconductor manufacturing apparatus **70** differs from the semiconductor manufacturing apparatus shown in FIG. **14** in that the apparatus **70** includes a liquid bath **73** that contains a DBE liquid. A PSZ supply tube **72** and a He supply tube **71** are inserted into the liquid bath **73**, and a tip end of the PSZ supply tube **72** and that of the He supply tube **71** are arranged below a liquid level of the DBE liquid.

Female connectors **75** are provided at tip ends of the He supply tube **71** and the PSZ supply tube **72**, respectively, and corresponding male connectors **85** having a valve are provided at the PSZ container **80**. By one-touch connection between the female connectors **75** and the corresponding male connectors **85**, the PSZ container **80** is connected to the He supply tube **71** and the PSZ supply tube **72**.

Attachment and detachment of the PSZ container **80** to and from the semiconductor manufacturing apparatus **70** are executed in the DBE liquid. Therefore, the air does not contact with the PSZ liquid. Since the DBE liquid is contained in the PSZ container **80** as a solvent for the PSZ liquid, no problem occurs even if a small amount of the DBE liquid is mixed into the PSZ container **80**.

Furthermore, the semiconductor manufacturing apparatus and the PSZ container **80** according to the fourth embodiment are also relatively inexpensive, and can be realized by simple changes in designs of the conventional semiconductor manufacturing apparatus and the conventional PSZ container, respectively.

A material for the PSZ container **80** may be a flexible material such as polyethylene in place of glass. When the PSZ container **80** consists of the flexible material and the air is mixed into the male connectors **85**, the air can be easily removed by an operator's compressing the PSZ container **80** by an operator's hand after the PSZ container **80** is dipped into the liquid bath **73**. It is noted that the DBE liquid does not flow backward into the PSZ container **80** since the respective male connectors **85** include valves.

Fifth Embodiment

FIG. **11** is a schematic diagram of a semiconductor manufacturing apparatus and a PSZ container **80** according to a fifth embodiment of the present invention. The fifth embodiment differs from the fourth embodiment in a shape of a liquid bath. **91**. Other constituent elements in the fifth embodiment may be identical to those in the fourth embodiment. A region R1 of the liquid bath **91**, into which a tip end of a He supply tube **71** and that of a PSZ supply tube **72** are inserted, is filled with a DBE liquid. Therefore, a PSZ liquid does not contact with not only the air but also a gas such as He.

A region R2 of the liquid bath **91** has an upper opening portion. The PSZ container **80** can be attached to the He supply tube **71** and the PSZ supply tube **72** by operator's inserting the PSZ container **80** into the liquid bath **91** from this opening portion. The liquid bath **91** includes a porthole **93**. The operator can, therefore, connect the PSZ container **80** to the He supply tube **71** and the PSZ supply tube **72** while viewing the liquid bath **91** from the porthole **93**.

Sixth Embodiment

FIG. **12** is a schematic diagram of a semiconductor manufacturing apparatus and a PSZ container **81** according to a sixth embodiment of the present invention. In the fourth and the fifth embodiments, the attachment and detachment of the PSZ container are executed in the DBE liquid. In the sixth embodiment, the attachment and detachment of the PSZ container are executed in a He gas atmosphere.

An upper portion of a region R1 of the PSZ container **81** is filled with the He gas. A liquid bath **92** includes a supply port **350** for supplying the He gas and an exhaust port **351** for exhausting the air or the like mixed into the liquid bath **92** together with the He gas. By so constituting, even if the gas other than the He gas is mixed into the PSZ container **81** while the PSZ container **81** is being replaced with another container **81**, the gas can be exhausted.

In the semiconductor manufacturing apparatus, a connector C3*a* is connected to a PSZ supply tube **312** through a valve **310**, and also connected to a balloon **360** through a valve **309**. A connector C4*a* is connected to a He supply tube **316**. The balloon **360** consists of, for example, a rubber having a high elasticity and a low reaction with the PSZ liquid. The balloon **360** is filled with the PSZ liquid in advance. A valve **307** is provided at the He supply tube **316**, and an exhaust tube **317** is connected between the valve **307** and the connector C4*a* through a valve **308**.

A PSZ outlet tube **321** and a He inlet tube **322** of the PSZ container **81** include two valves **304** and **306** and two valves **303** and **305**, respectively. Connectors C3*b* and C4*b* of the PSZ outlet tube **321** and the He inlet tube **322** are formed to be directed downward. The PSZ outlet tube **321** from the PSZ container **81** to the valve **304** is filled with the PSZ liquid in advance, and a piping between the valves **303** and **305** and a piping between the valves **304** and **306** are each filled with a pressurized He gas in advance.

An operation for attaching the PSZ container **81** to the semiconductor manufacturing apparatus will be described. The PSZ container **81** is moved into the liquid bath **92** so that the connectors C3*b* and C4*b* are provided in the He gas atmosphere in the region R1 (at a step S**300**). At this time, the air may possibly remain in a piping from the valve **306** to the connector C3*b* and a piping from the valve **305** to the connector C4*b*. Considering this, by opening the valves **305** and **306**, the pressurized He gas is ejected (at a step S**310**). By doing so, the air is discharged to the outside of the connectors C3*b* and C4*b*. Since the air is higher in specific gravity than the He gas, the air is moved to a liquid level of the DBE liquid and exhausted from the exhaust port **351**.

Thereafter, the connector C3*a* is connected to the connector C3*b* and the connector C4*a* is connected to the connector C4*b* (at a step S320). At this time, the valves **307**, **308**, **309**, and **310** are closed. The valves **309** and **308** are then opened in this order (at a step S330). The balloon **360** filled with the

PSZ liquid is thereby contracted and the He gas residing in a piping from the valve **304** to the valve **309** is returned into the PSZ container **81**.

After closing the valves **308** and **309** in this order, the valves **307** and **310** are opened in this order (at a step S**340**). The He supply tube **316** thereby supplies the He gas into the PSZ container **81** and the PSZ liquid is supplied to a discharge portion through the PSZ supply tube **312**.

When the PSZ container **81** is to be detached from the semiconductor manufacturing apparatus, then the valve **310** is closed, and the valve **309** is closed after the balloon **360** is filled with the PSZ liquid to some degree. After closing all the valves **303** to **308**, the PSZ container **81** is detached.

According to the fifth embodiment, the PSZ container **81** can be replaced by a new PSZ container **81** in an environment shut off from the air while preventing mixture of the He gas.

As described above, in the embodiments, it is preferable that the PSZ liquid is discharged onto a dummy wafer before being coated on a desired wafer. This is because the DBE liquid may possibly enter the PSZ container **81** during the replacement.

The embodiments may be executed in combination. For example, the PSZ container **50** shown in FIGS. **7** and **8** can be applied to any one of the first and the third to the fifth embodiments.

FIG. **13** is a table that shows effects of the respective embodiments. In the table of FIG. **13**, the numbers of particles generated when the PSZ liquid is coated on the semiconductor substrate at the SOG step are shown. In the conventional technique shown in FIG. **14**, many particles having respective particle diameters are generated. In the first to the sixth embodiments, particles having particle diameters of 0.2 to 1.0 μm are hardly generated. According to the embodiments of the present invention, therefore, it is expected to improve the yield of semiconductor devices.

In the respective embodiments of the present invention, the coating liquid is not limited to the PSZ liquid but may be any coating liquid for forming a silica-containing film or the like.

The invention claimed is:

1. A semiconductor manufacturing method using a semiconductor manufacturing apparatus comprising a discharge portion discharging a coating liquid onto a substrate; a gas supply tube pressurizing an interior of a liquid container with an inert gas; a coating liquid supply tube airtightly supplying the coating liquid from the liquid container to the discharge portion using pressurization from the gas supply tube; a first connecting portion capable of attaching and detaching the liquid container to and from the coating liquid supply tube; a second connecting portion capable of attaching and detaching the liquid container to and from the gas supply tube; an exhaust tube capable of reducing an internal pressure of the coating liquid supply tube including the first connecting portion; and a solvent supply tube supplying a solvent, which can dissolve the coating liquid, to the first connecting portion;

the method comprising:

- attaching the liquid container to the first connecting portion and the second connecting portion;
- supplying the inert gas to the liquid container via the gas supply tube, thereby carrying the coating liquid to the discharge portion via the coating liquid supply tube;
- discharging the coating liquid to the substrate from the discharge portion;
- reducing an internal pressure of the liquid container via the exhaust tube and the second connecting portion after discharging the coating liquid; and
- returning the coating liquid in the first connecting portion and the liquid supply tube to the liquid container by using the pressure in the liquid container,

the method further comprising:

- supplying the solvent to the first connecting portion and to the coating liquid supply tube, therewith returning the coating liquid in the first connecting portion and the liquid supply tube to the liquid container.

2. The semiconductor manufacturing method according to claim **1**, wherein

the coating liquid is a perhydropolysilazane liquid, and

the solvent capable of dissolving the coating liquid is a dibutyl ether.

3. A method of manufacturing a semiconductor device using a semiconductor manufacturing apparatus comprising:

- a discharge portion discharging a coating liquid onto a semiconductor substrate;
- a liquid container containing the coating liquid;
- a gas supply tube pressurizing an interior of the liquid container with an inert gas;
- a coating liquid supply tube airtightly supplying the coating liquid from the liquid container to the discharge portion using pressurization from the gas supply tube;
- a first connecting portion capable of attaching and detaching the liquid container to and from the coating liquid supply tube;
- a second connecting portion capable of attaching and detaching the liquid container to and from the gas supply tube;
- an exhaust tube capable of reducing an internal pressure of the interior of the liquid container through the second connecting portion;
- a first valve opening or closing between the first connecting portion and the liquid container;
- a second valve opening or closing between the second connecting portion and the liquid container; and
- a solvent supply tube supplying a solvent, which can dissolve the coating liquid, to the first connecting portion;

the method comprising:

- carrying the coating liquid to the discharge portion through the coating liquid supply tube by supplying the inert gas to the liquid container through the gas supply tube;
- discharging the coating liquid to the substrate from the discharge portion;
- after discharging the coating liquid, reducing an internal pressure of the liquid container through the exhaust tube, the second connecting portion and the second valve, in a state of closing the first valve and opening the second valve;
- returning the coating liquid in the first connecting portion and the liquid supply tube to the liquid container by using the reduced internal pressure in the liquid container, and supplying the solvent from the solvent supply tube to the first connecting portion and the liquid supply tube, in a state of closing the second valve and opening the first valve;
- connecting the gas supply tube to the liquid supply tube;
- flowing the solvent in the liquid supply tube and the first connecting portion to the liquid container by supplying the inert gas to the liquid container through the liquid supply tube; and
- detaching the liquid container from the first and the second connecting portions after closing the first and the second valves.

4. The semiconductor manufacturing method according to claim **3**, further comprising:

attaching the liquid container to the first and the second connecting portions;

reducing an internal pressure of the coating liquid supply tube and the first connecting portion through the exhaust tube in a state that the first and the second valves are closed;

supplying the coating liquid from the liquid container to the coating liquid supply tube and the first connecting portion by using the reduced internal pressure in the coating liquid supply tube after opening the first valve;

mixing the solvent from the solvent supply tube with the coating liquid in the coating liquid supply tube;

supplying the mixture liquid of the coating liquid and the solvent to the discharge portion by using a pressurization from the gas supply tube after opening the first and the second valves; and

supplying the coating liquid in the liquid container to the discharge portion.

5. The semiconductor manufacturing method according to claim **3**, wherein the coating liquid is any coating liquid for forming a silica-containing film.

6. The semiconductor manufacturing method according to claim **3**, wherein the solvent capable of dissolving the coating liquid is a dibutyl ether.

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